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NATIONAL EMISSIONS INVENTORY OF SOURCES AND EMISSIONS OF MOLYBDENUM

GCA Corporation

PREPARED FOR
Environmental Protection Agency

May 1973

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A national inventory of the sources and emissions of the element molybdenum was conducted. All major sources of molybdenum-containing emissions were identified and their molybdenum emissions into the atmosphere estimated. Also, a method for updating the results of the study every two years was recommended.

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by

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GCA Technology Division
Bedford, Massachusetts 01730

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EPA Project Officer: David Anderson

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
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ABSTRACT

A national inventory of the sources and emissions of the element molybdenum was conducted. The study included the preparation of an overall material flow chart depicting the quantities of molybdenum moving from sources of mining and importation through all processing and reprocessing steps to ultimate use and final disposition. All major sources of molybdenum-containing emissions were identified and their molybdenum emissions into the atmosphere estimated. A regional breakdown of these sources and their emissions was also provided. The physical and chemical nature of the molybdenum-containing emissions was delineated to the extent that information was available, and a methodology was recommended for updating the results of the study every two years.

I. INTRODUCTION

A. PURPOSE AND SCOPE

The Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards of the U.S. Environmental Protection Agency (EPA) has contracted with GCA Technology Division to conduct a national inventory of the sources and emissions of the element molybdenum. The purpose of the study was to define as accurately as possible, based on existing and available published and unpublished information, the levels, nature and sources of molybdenum containing emissions for defined geographic regions throughout the United States.

The scope of this program is outlined below:

- Develop an overall material flow chart depicting the quantities of molybdenum moving from sources of mining and importation, through all processing and reprocessing steps to ultimate use and final disposition as far as the movements can be treated.
- Identify all major potential molybdenum containing emission sources, and estimate the total quantity of molybdenum emitted to the atmosphere from each source. Emission factors, level, and types of air pollution control will also be provided for each of these sources to the extent that available information permits.
- Define those sources which contribute at least 80 percent of the total emissions of molybdenum.
- Provide a regional breakdown of these major sources and their emissions.
- Present the nature of the molybdenum containing emissions for each of these major sources including a delineation of their physical and chemical form and particle size distribution to the extent that information is available.
- Provide recommendations as to a methodology for updating the results of this study every two years.

B. CONCLUSIONS

1. Material Flow

Based on all available data, 34,821 tons of molybdenum were consumed in the U.S. in 1970. The sources of molybdenum were imports, releases from government stockpiles, and domestic mining.

A major portion of the molybdenum ore concentrate was converted to the oxide. Most of the oxide was consumed in making steel and other alloys, with only a small portion being used for pigments, catalysts, lubricants, and other miscellaneous products.

2. Principal Emission Sources

Two thirds of the estimated atmospheric emissions of molybdenum are not associated with the molybdenum industry, but result from the combustion of coal. Coal is far the largest source of emissions. Despite a relatively small concentration of molybdenum in coal, there was sufficient quantity of coal burned to produce about 610 tons of emitted molybdenum in 1970.

Within the molybdenum industry, several sources were identified as being of approximately similar consequence: the mining of ore; the production of ferromolybdenum; the production of steel containing molybdenum as an alloying ingredient; and the roasting of ore concentrate. Together these are estimated to produce about 29% of all U. S. emissions.

3. Regional Emissions

The region of the U. S. in which most of the molybdenum is estimated to be emitted is Region 5* (Ohio and vicinity). This is partly due to the large emission from coal combustion. In the absence of this, the molybdenum industry alone would produce the largest total emission in Region 9, princpally Arizona, based on certain assumptions set forth in Chapter IV.

*See page 18 for a list of regions.

4. Nature of Emissions

Based on the physical properties of molybdenum and its compounds, most of its emissions are estimated to be in particulate form ranging from submicrometer to micrometer sized particles. The chemical forms are believed to be largely simple oxides and sulphides, with little elemental molybdenum being emitted.

5. Degree of Control

The overall level of control of molybdenum emission is estimated to have been about 86 percent in 1970. The degree of control would have been greater, but for the relatively poor control of coal flyash (82 percent estimated), which sharply lowered the overall average.

II. OVERALL U. S. MATERIAL FLOW CHART FOR MOLYBDENUM - 1970

The molybdenum industry uses mining, co-product, and import sources of molybdenum disulphide concentrate. This material, for the most part, is roasted to molybdenum oxide, most of which is consumed in steelmaking and other metallurgical processes. The industry is described in more detail below and in Section III. Figure 1* presents a flow diagram depicting the total quantities of molybdenum products moving from sources through the processing and reprocessing steps to ultimate use and final disposition.

A. U. S. PRODUCTION AND ORE PROCESSING

Molybdenum is produced in the U. S. both as a primary yield and as a co-product yield from copper, tungsten, and uranium operations. Of the 55,676 tons of molybdenum produced from these sources in 1970, 68 percent was as a primary yield. The primary ore contains typically only 0.3 percent molybdenum disulphide, and thus requires extensive beneficiating operations including flotation. Similar beneficiating processes are used in producing co-product concentrates.(1)

B. IMPORTS AND EXPORTS OF MOLYBDENUM CONCENTRATE

Due to high import tariffs for molybdenum products and a self-sufficiency in production, only 12 tons were imported into the United States in 1970. Total exports of ore and concentrates totaled 27,800 tons of contained molybdenum.(1)

C. GOVERNMENT AND INDUSTRIAL STOCKPILES CHANGES

The Bureau of Mines(1) reports that inventories of industrial stocks increased by 658 tons in 1970. GCA, however, in their preparation of Figure 1, estimates a decrease of 4,533 tons in industrial stockpiles in order to supply the necessary raw material for reported consumption levels. The National Government Stockpile was reduced by 2,400 tons in 1970.(1)

*Note. Data in Figure 1 and in this section are left unrounded, for purposes of information control. On the average, the typical statistic is accurate to within 10%, in the opinion of the investigators.

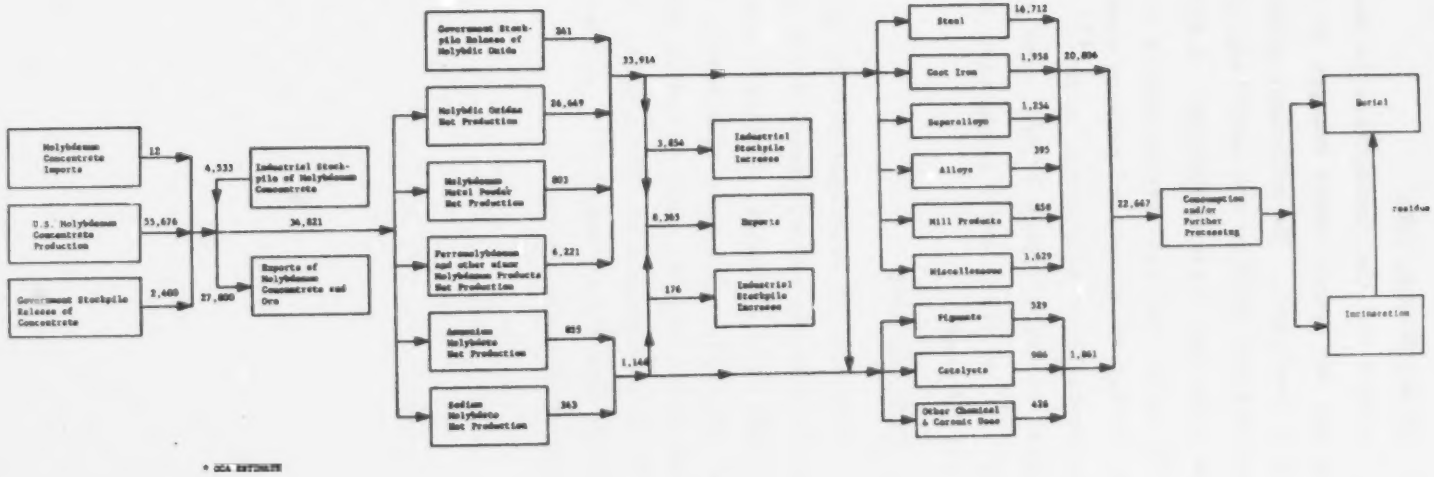

Figure 1. Molybdenum 1970 Material Flow
(tons contained in Mo)

D. METALLURGICAL USES

Almost all the concentrate is roasted to the oxide except for a very minimal amount which remains as the sulfide and is purified for use as a lubricant. The principal primary products from the roasted concentrate used by the metallurgical industries are molybdenum oxide and ferromolybdenum. A small amount of metal power, about 3% of total, was used predominantly in mill products.(1) Almost 90 percent of exports of primary products (8,365 tons) were roasted concentrate or molybdenum oxide.(1) The domestic use by the metallurgical industry totals 20,806, tons or 91.7 percent of domestic molybdenum.(1) Of this, steel production is by far the major consumer (71 percent).

E. CHEMICAL USES

Although the principal primary product used in the chemical industries is molybdic oxide, ammonium and sodium molybdates are used in the production of pigments, catalysts and other miscellaneous chemicals. In 1970, 1,342 tons of molybdic oxide, 805 tons of ammonium molybdate and 343 tons of sodium molybdate were used to produce 529 tons of pigments, 906 tons of catalysts, and 426 tons of other products (mainly ceramics).(1) All weights expressed are in terms of contained molybdenum content.

III. SOURCES AND ESTIMATES OF MOLYBDENUM - CONTAINING EMISSIONS

A. DATA PRESENTATION AND ACCURACY

Table 1 presents a summary of the data from which emissions were estimated for all major potential sources. Each of the columns comprising this table will be discussed below.

1. Emission Factors

Except where indicated, this gives the pounds of total particulates emitted per ton of production. Such considerations as:

- variations in process conditions among individual plants comprising a source category
- inaccuracies in existing data
- a limited quantity of existing data,

may, however, result in an average emission factor for a source category varying by more than an order of magnitude from the value presented. In recognizing the need to indicate the level of accuracy of these emission factors, a reliability code is presented along with each emission factor value appearing in the Table. This reliability code system is described below and is based on the system utilized in EPA Document No. AP-42, "Compilation of Air Pollutant Emission Factors":

A: Excellent

This value is based on field measurements of a large number of sources.

B: Above Average

This value is based on a limited number of field measurements.

C: Average

This value is based on limited data and/or published emission factors where the accuracy is not stated.

D: Below Average

This emission factor is based on engineering estimates made by knowledgeable personnel.

TABLE I

SOURCES AND ESTIMATES OF MOLYBDENUM-CONTAINING EMISSIONS

Source	Uncontrolled Particulate Emission Factor (lb/ton)	Uncontrolled Particulate Emission Factor (kg/kgx10^3)	Reliability Code	Production Level (tons/yr)	% Mo in Emissions	Mo Emissions Before Controls (tons/yr)	Estimated Level of Emissions Control	Mo Emissions Following Controls (tons/yr)
MINING								
Open Pit	10	15	D	13,000	*	65	0	65
Underground	0.5	0.25	D	25,986	*	6	0	6
Copper Open Pit	10	5	D	16,690	*	83	0	83
BENEFICIATION	52	26	D	34,821	*	906	98.8%	11
ROASTING	100	50	C	34,821	*	1,740	98%	35
METALLURGICAL								
Ferromolybdenum-Electric Arc	200	100	D	6,221	*	622	90%	62
Molybdenum Metal	2000	1000	B	803	*	803	99.9%	1.0
CHEMICAL PRODUCTION	Nil	Nil		1,148	*	Nil	Nil	Nil
STEEL & ALLOY PRODUCTION								
Steel	25	12.5	C	14,712	*	184	78%	41
Cast Iron	15	7.5	C	1,958	*	15	99%	0.1
Super Alloys	200	100	C	1,254	*	126	78%	28
Alloys	25	12.5	C	395	*	5	78%	1
Mill Products	0.5	0.25	C	858	*	0	-	0

TABLE I (cont.)

Source	Uncontrolled Particulate Emission Factor (lb/ton)	Uncontrolled Particulate Emission Factor ($kg/kg \times 10^3$)	Reliability Code	Production Level (tons/Yr)	% Mo in Emissions	Mo Emissions Before Controls (tons/yr)	Estimated Level of Emissions Control	Mo Emissions Following Controls (tons/yr)
NON-METALLURGICAL USES	2	1	D	1,861	*	2	0	2
INADVERTENT SOURCES								
Coal burning	NA	NA		33,800,000 (uncontrolled emissions)	.01 (B)	3,380	82%	610
Oil combustion	NA	NA		287,000 (uncontrolled emissions)	.01 (C)	29	0	29
Mineral Processing	NA	NA		6.9×10^6 (controlled emissions)	.00023 (D)	16	NA	16
TOTALS						7,179	86%	990

NOTE: NA = Not Applicable

*Emission factor multiplier equal to tons of Mo processed annually

2. Level of Production Activity

This column depicts the quantity of material produced (unless otherwise stated) annually. When multiplied by the emission factor an estimate of the total particulate emissions for that source in lbs per year is obtained.

The values in this column are based on the material flow calculations presented in Section II. Consequently, they have the same accuracy as those material flow values which is estimated at ± 10%.

3. Percent Metal in Emissions

The method of analyzing or assaying a dust sample for the amount of metal it contains determines to a large extent the reliability of the data. For example, analytical chemistry techniques for dust containing substantial fractions of metal can be accurate to within a small percentage. On the other hand, optical spectroscopy methods for determining concentrations on the order of parts per million can be inaccurate by a factor of 2. Because of this variability, the reliability codes discussed above for the emission factors are also utilized to estimate the relative accuracy of the percentage values listed in Column III.

4. Level of Emissions Before Control

The values in this column are derived by multiplying the values in columns 1-3. The result is converted to tons/year of emissions before control.

5. Estimated level of Emission Control

The overall effectiveness of control for a source category is based on two factors:

- the portion of the processes which are under control
- the typical degree of control

For example if 60% of vertical roasters have some type of particulate emission control, and these include both scrubbers and precipitators

such that the apparent weighted average efficiency of control is 85%, the overall control effectiveness is estimated to be 60 x 85 = 51%.

The accuracy of control efficiency data varies with the degree of control. For a wet scrubber operating at 80% efficiency, i.e. passing 20% material, the actual emission may safely be assumed to be between 15 and 25% because of the relative ease of making determinations at this level. Thus the emissions after control may be assumed to be accurate within ± 5/20 or 25%. On the other hand, for a baghouse reported as being 99% efficient, or passing only 1% of the material, the actual emission may vary from 0.5 to perhaps 2% because it is frequently difficult to make low-level measurements with accuracy. In such case, the resulting emission data could be in error by a factor of 2.

Unless otherwise specified, it is assumed that the reported overall level of particulate control applies equally to all molybdenum-containing particles, independent of size, resistance and other important collection parameters. This assumption results in a correct estimate of molybdenum emissions after control when the particulate is chemically homogenious, i.e. molybdenum is contained in the same concentration in all particles. If however, molybdenum is concentrated in certain particles and in addition the efficiency of the control equipment is not uniform for all particles, then the utilization of an average control level is less valid for calculating molybdenum emissions after control. Data on the preferential control of molybdenum-containing particles is seldom available, but is included in this report when possible.

The accuracy of estimating the level of control for a specific source category is dependent on the quality of available data. The investigators feel that, in general, the level of control data will contribute an accuracy to the resulting emission estimates within ± 25 percent.

6. Level of Metal Emissions After Control

The values in this column are derived by multiplying

the values in Column 4 by the value (100 minus estimated Level of Control).

B. DEVELOPMENT OF EMISSIONS ESTIMATES - 1970

Estimates of particulate emissions containing molybdenum in the U. S. atmosphere are developed in the following paragraphs and in Table 1. The Table indicates that a substantial portion of the emissions is due to inadvertent sources, i.e. those not directly a part of the molybdenum industry.

1. Mining

Molybdenum ore is presently recovered from mines as a major ore and as a byproduct or co-product from copper, tungsten and uranium mining. The only significant sources of ore are the molybdenum and copper mines.[2,3] The ore is presently recovered by both open-pit and underground methods. The portion of production from each method shifts significantly from year to year and present trends indicate an increase in open-pit excavation in the future.

In 1970, of the 55,676 tons of molybdenum contained in concentrate mined, 24 percent (13,000 tons) is estimated to have come from non-copper open pit mines, 46 percent (25,986 tons) from underground molybdenum mines, and 30 percent (16,690 tons) from open pit copper mining. The emission factors used in Table 1 are based on emission factors for other similar operations.[4] The resulting estimate is that 154 tons of molybdenum were released by mining of all types in 1970.

2. Beneficiation Operation

Due to the low concentrations of MoS_2 in the ore (0.3% average), beneficiation to a concentrate is necessary before comsumption. The operations involved include crushing, grinding, classification, flotation, filtration and drying. Recovery from copper ore is generally of the same nature; however, different flotation agents are used due to the necessity of also maximizing the recovery of the copper. Recovery from ore generally runs between 70 and 90 percent although recovery from copper ore has been reported as low as 50 percent. The

concentrate itself is about 98 percent MoS_2. Although no data were found on emissions from beneficiation, the general procedures are wet, except for material handling, crushing, and drying. Emissions from handling and crushing are frequently estimated for other industries at 2 lbs/ton of feed and, in the case of molybdenum, are estimated to be controlled at 95 percent.[4] The same identical emission factor can be reasoned to yield lbs. of molybdenum emitted per ton of molybdenum produced, assuming the emitted particles contain the same concentration as the feed. Emissions from drying processes in other industries are generally on the order of 50 lbs. per ton of feed and are typically well controlled at about 99 percent.[4] The resulting emissions for handling and crushing are 50 tons and for drying 1240 tons. After control, emissions are estimated at 15 tons/yr.

3. Roasting Concentrate

Virtually all MoS_2 concentrate is roasted to the oxide before consumption. A minor amount is purified and used as a lubricant, but neither the quantity of material not the estimated emissions are significant. All roasting in 1970 was accomplished by multiple hearth Nichols-Herschoff furnaces, although more recently these are being replaced by fluid bed roasters in the copper industry. The latter method will be expected to generate more emissions until the point of control.

An emission factor of 168 lbs. of particulate per ton of metal is reported for multiple hearth furnaces in the copper industry[4] which is equivalent to 100 lbs. of molybdenum per ton of molybdenum, assuming the particulate is MoS_2. Since approximately 34,821 tons of molybdenum in concentrate form was roasted, this gives an emission of 1,740 tons before control. Reference (4) indicates a control effectiveness of 85 percent for copper roasting. However, discussion with the molybdenum industry suggests that a better estimate of molybdenum roasting control is 98 percent, producing a net emission of 35 tons.[5]

4. Ferromolybdenum Production

Production of ferromolybdenum amounted to approximately 6,221 tons in 1970, or about 18 percent of the molybdenum consumption. Molybdenum oxide is the raw material for making ferromolybdenum. Two processes are in use, electric arc furnaces, and a silico-thermite process. For the former, emissions factors and controls applicable to a variety of ferroalloy production processes indicate typical values of 200 lbs/ton and 80 percent control efficiency.[4] In the four years since these control estimates were made, however, we believe that the level of control for ferromolybdenum production has improved to at least 90 percent. For the silico-thermite process, no information was found. It is suspected that the process generates substantially more emission initially but is enclosed to a greater extent and under better emission control. It is assumed that 200 lbs/ton and 90 percent control apply effectively to the entire ferromolybdenum production, giving an estimated emission of 70 tons after control.

Slag from some ferromolybdenum furnaces is crushed, a process which produces some emissions. In one instance, the material is crushed to 320 mesh (about 50 microns) with a substantial portion of the material finer than this. The material is dry, and is used for landfill. The molybdenum content of slag, and emissions factors, were not available. This source is assumed to be of negligible consequence relative to the major sources listed in Table 1.

5. Molybdenum Metal Production

About 2.3 percent of the roasted concentrate was used to produce metallic molybdenum. Two processes were used, the more common being the reduction of MoS_2 in a hydrogen atmosphere. The molybdenum sublimes and is carefully collected as a fine power. It is subsequently sintered in various forms for ultimate use. The second process produced a higher purity metal, by reducing ammonium molybdate in an electric furnace. An emission estimate was made by assuming that 100 percent of the material is emitted initially, and that control is an

excellent 99.9 percent. This results in an estimated 1.0 ton of molybdenum emitted to the atmosphere.

6. Chemical Molybdates Production

About 3 percent of the roasted concentrate was used to produce compounds of molybdenum. The production of sodium molybdate and ammonium molybdate is accomplished by dissolving molybdic oxide in either sodium hydroxide or ammonium hydroxide, precipitation, recrystallization and drying. Calcium molybdate is produced by mixing pulverized limestone with molybdic oxide to produce a product analyzing 46.3 to 46.6 percent molybdenum. Mo emissions primarily would be from handling, and are assumed to be negligible.

7. Steel and Alloy Production

About 57 percent of the U. S. molybdenum was consumed in the production of steel, cast iron, and various alloys (Figure 1). The emissions from these processes have apparently not been analyzed in in any detail for molybdenum content, however. One approach to making estimates is to assume that the emissions will contain the same percentage of molybdenum as the feed. This is partly justified by the fact that the vaporization temperature of molybdenum is at least 3700°C, far above the operating temperature of all types of furnaces with the possible exception of an electric arc furnace. This means that molybdenum should not be concentrated in the emission particulate. There is no apparent reason for the particulate to be low in molybdenum content, either. Therefore, it is assumed that the emission factor of pounds of molybdenum per tons of molybdenum feed, is the same as the emission factor of pounds of particulate per ton of steel, alloy, etc., produced. These are given in Table 1 along with control effectiveness factors for the various processes. The total emission estimate after control is 70 tons, of which steels and super alloys are estimated to be responsible for the greatest proportion as shown in Table 1.

8. Non-Metallurgical Uses

About 8 percent of all molybdendum is used for pigments,

catalysts, and other chemical and ceramic purposes. Emisssions from these sources are believed to be almost entirely from material handling. Using a typical emission factor of 2 lbs/ton, the emissions are shown in Table 1 to be negligible.

9. Inadvertent Sources

a. Coal Combustion

Coal consumption in 1970 amounted to about 517,000,000 tons.[12] The particulate generated has been estimated at 33,800,000 tons of which 82% was controlled.[4] The concentration of molybdenum in coal ash has been reported as 0.011 percent (73 samples of Appalachian coal ash, spectrographic analyses),[6] as 0.003 percent (13 samples of coal ash, semiquantative determinations)[7] and as about .002 percent (17 samples of flyash).[8] The weighted average is about 0.01 percent, resulting in a net molybdenum emission after control of 610 tons.

b. Oil Combustion

The concentration of molybdenum in residual oil ash has been reported as 0.00093 (at least 3 samples of ash)[9] and as 0.025 (two samples of ash),[10] giving an average of about 0.01 percent, the same as for coal. (See also Reference 11 for variations.) An estimated 287,000 tons of oil ash particulate is generated[4] which is practically not controlled. This results is an estimate of about 29 tons of molybdenum released to the atmosphere.

c. Non-Ferrous Minerals

A large quantity of rock, cement, fertilizer, clay, and lime dust is released into the atmosphere in the U. S., estimated to be 6,900,000 tons after control. No data on the concentration of molybdenum in these dusts has been found, however. The earth's crust is estimated to contain about 2.3 ppm of molybdenum.[11] If this concentration applies to the mineral emission above, 16 tons of molybdenum would be the estimated emission. This first approximation is included in Table 1.

C. SUMMARY OF PRINCIPAL EMISSIONS

Table 2 summarizes the major sources and estimated emissions of molybdenum, as developed in Table 1 and accompanying discussion. The sources are grouped in two categories; those directly originating with the molybdenum industry or industries using molybdenum, and those having no relationship to the molybdenum industry, called inadvertent sources. Due to the content of molybdenum in coal, the latter category is larger.

These prinicpal estimates are examined further in later sections of this report.

TABLE 2

SUMMARY OF PRINCIPAL SOURCES AND EMISSIONS OF MOLYBDENUM

Inadvertant Sources	U.S. Tons/year of Mo.	% of U.S.
Coal combustion	610	61.6
Molybdenum Industry Sources		
Mining, copper open pit	83	8.4
Mining, Molybdenum open pit	65	6.6
Ferromolybdenum production	62	6.3
Steel production using Molybdenum	41	4.1
Roasting concentrate	35	3.5
		90.5

IV. REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

For purpose of showing geographical distribution, the U.S. was divided into ten regions identical to the Regional Branches of EPA:

Region	State
I	Conn., Me., Mass., N.H., R.I., Vt.
II	N.J., N.Y., P.R., V.I.
III	Del., Md., Pa., Va., W.Va., D.C.
IV	Ala., Fla., Ga., Ky., Miss., N.C., S.C., Tenn.
V	Ill., Ind., Mich., Minn., Ohio, Wis.
VI	Ark., La., N.M., Okla., Texas
VII	Iowa, Kans., Mo., Nebr.
VIII	Colo., Mont., N. Dak., S. Dak., Utah, Wyo.
IX	Ariz., Calif., Nev., Hawaii and the So. Pacific
X	Alaska, Idaho, Oreg., Wash.

Emissions from the principal emission sources listed in Table 2 are distributed among these ten regions, as shown in Table 3. Also, the number of plants producing the emissions is shown in the table when such information was available.

The accuracy of the distribution by region varies with the category. The number of plants per category varied from 1 to several thousand in this study. When the number of plants was less than 100, an attempt was made to identify each plant and plant location, and include it in one of the ten regions. When production or capacity figures for these plants were available, total production or capacity for each region was computed, and the U.S. emission estimate for that category was distributed by region accordingly. When production or capacity figures were not available, the emissions were distributed by the number of plants in each region. If the number of plants was very small or there was reason to believe that certain plants were larger or produced more emission, distributions were weighted accordingly.

When the estimated number of plants was greater than 100, and the distribution of plants was not known, the regional breakdown was made on a different basis, such as population, geographical area, or shipments reported as most appropriate for that category. Whether the distribution was by plant size, number of plants, or another statistic, the distribution is believed to be accurate to within 10 percent in most cases.

The emission estimates listed in Table 2 are distributed in Table 3 on the following basis:

Coal combustion: proportional to coal shipped by state of destination

Mining, copper pit: 14 mines, assumed to have equal emissions

Mining, molybdenum open pit: two mines, assumed to have equal emissions

Ferromolybdenum: five companies at five locations, assumed to have equal emissions

Steel production: 41 companies producing molybdenum alloys, and stainless and tool steels containing molybdenum; assumed to have equal emissions

Roasting concentrate: nine companies at nine locations, assumed to have equal emissions.

The overall distribution of emissions by region is shown in Table 3, along with the distribution of plant sources. Region 5 is estimated to have the largest total emission of molybdenum, followed by Region 3 (approximately that area bound by Pennsylvania, Virginia, and Illinois). However, this appearance is partly due to the large amount of molybdenum emitted with coal flyash. In the absence of this large source, Region 9 (mostly in Arizona) would be estimated to produce the largest emission, with Region 3 next.

Considering the geographical areas of these regions, Region 3 has the most concentrated emissions, with .0019 tons of molybdenum emitted to the atmosphere per square mile-yr.

TABLE 3

REGIONAL DISTRIBUTION OF PRINCIPAL SOURCES AND EMISSIONS

Principal Sources	EPA REGION										Total (Units)	Reference
	1	2	3	4	5	6	7	8	9	10		
Inadvertent Sources												
Coal Burning	0.7	5.7	21.8	21.1	41.3	1.4	4.1	3.3	0.7	0.3	100% (Coal Shipped	
	4.3	34.8	133	129	249	8.6	25	20	4.3	1.7	610 (TPY)	12
Molybdenum Industry Sources												
Mining, Copper	0	0	0	0	0	1	0	1	12	0	14 (Mines)	
	0	0	0	0	0	6.0	0	6.0	71.0		83 (TPY)	12, 13
Mining, Molyb.	0	0	0	0	0	1	0	1	0	0	2 (Mines)	
	0	0	0	0	0	32.5	0	32.5	0	0	65 (TPY)	12, 14
Ferromolyb.	0	1	4	0	0	0	0	0	0	0	5 (Plants)	
	0	12	50	0	0	0	0	0	0	0	62 (TPY)	15
Steel Prod'n	1	7	18	0	13	0	0	0	1	1	41 (Companies)	
	1	7	18	0	13	0	0	0	1	1	41 (TPY)	16
Roasting	0	1	2	0	1	0	0	2	3	0	9 (Plants)	
	0	4	8	0	4	0	0	8	11	0	35 (TPY)	15
TOTAL	5	58	209	129	267	47	25	66	87	3	896 (TPY)	
	0.5	5.9	21.1	13.0	27.0	4.7	2.5	6.7	8.8	0.3	90.5 % of U.S.	

V. NATURE OF EMISSIONS

Very little data describing the physical or chemical properties of the molybdenum-containing particulate were obtained. Some deductions regarding the probable character of the emissions may be drawn from the physical properties of molybdenum and its compounds which are presented in Table 4 and Figure 2.

TABLE 4

PHYSICAL PROPERTIES OF MOLYBDENUM AND COMPOUNDS (*)

	Molybdenum	Mo_2O_3	MoS_2
Melting Point	2610 °C	(sublimes)	(sublimes)
Boiling Point	5560 °C	1155 °C	450 °C
Density	10.2 grams/cm^3	--	--
Atomic Weight	95.94 a.w.u.	240 a.w.u.	160 a.w.u.
Heat of Vaporization	128 kg-cal/g-atom	--	--
Hardness (Std. Minerology Scale)	--	--	1.2

* Perry's Chemical Engineers Handbook, 4th Edn, Table 3-169 (Ref. 17)

For example, flyash is the result of combustion temperatures in the vicinity of 1700°C. The metal molybdenum begins to oxidize above 20°C in air, and at 600°C oxidizes rapidly to MoO_3 especially in the presence of SO_2.[17] Thus it is doubtful that any molybdenum in elemental form is released in the combustion of coal. The oxide and the sulphide forms sublime well below the combustion temperature of coal, and consequently may be expected to be released either as extremely small particles or molecules of oxide or sulphide; or as condensed thin layers on the surface of other larger flyash particles.

Molybdenum in sulphide form is mined in extremely small concentrations. Dust emitted in mining is expected to consist of the

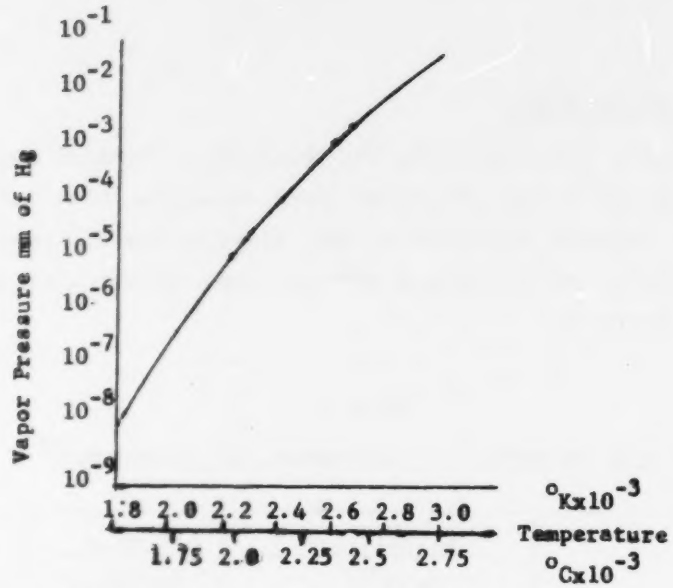

FIGURE 2

VAPOR PRESSURE OF MOLYBDENUM IN VACUUM versus TEMPERATURE (18)

APPLICATIONS OF MOLYBDENUM

POWDER

(1) Spray metallizing
(2) Glass to ceramic seals
(3) Alloy additions
(4) Specialized melting techniques

PRESSED AND SINTERED INGOTS

(1) Machined parts
(2) Forged parts
(3) Consumable vacuum arc-cast electrodes
(4) Contact disks
(5) Alloy additions
(6) Special forms such as rings, boats, etc.

SHEET

(1) Heat radiation shields
(2) Arch supports for high-temperature furnaces
(3) Boats for heat treating and process equipment
(4) Stamped, deep drawn and spun parts, anodes and other elements for electronic tubes
(5) Stampings for semi-conductor application
(6) Aircraft and missile structural and surface parts
(7) Electronic tube cathode sleeves

ROD

(1) Electronic tube leads - where glass to metal vacuum seal required
(2) Internal supports for vacuum tubes
(3) Contact disks for "make or break circuits"
(4) Machined parts
(5) Welding electrodes
(6) Electrodes and stirring rods in glass manufacture

WIRE

(1) Grid and internal supports for electronic tubes
(2) Support parts in lamps (hook and anchor wire)
(3) Mandrel for winding tungsten coils
(4) Wire cloth
(5) Furnace heating elements
(6) Thermocouples
(7) Spray bonding bearing and heat resistant surfaces
(8) Electrode wire for glass to metal seals

common rock with included or attached MoS_2. Since the sulphide is soft, it is not expected to fracture to fine particles. Possibly for this reason most of the dust emitted in mining will consist of rock, with most of the MoS_2 remaining behind in larger particles.

In the production of ferromolybdenum, and in the production of steel alloys containing molybdenum, the comments made above in discussing the combustion of coal are partly applicable. However, oxygen and sulphurous gases are relatively deficient in these metallurgical operations, and molybdenum is less apt to oxidize and then sublime as a fume. It is more probable that particulate emitted from these processes will contain entrapped molybdenum in metallic form. The molybdenum will partially oxidize following emission, and remain relatively stable as an oxide.

Roasting operations, at temperatures up to about 700°C, must produce some MoS_2 fume since the concentrate material begins to sublime at about 450°C. Probably a portion of these fumes will oxidize following emission. Thus, particulate emissions from roasting operations are expected to consist of submicrometer particles in both the sulphide and oxide forms.

One other source of emissions, developed in Table 1 but excluded in the list of principal sources, is oil burning, which produces submicrometer and micrometer sized particulate. A substantial portion of the nation's sub-micrometer particulate containing molybdenum may be expected to originate in the combustion of residual oils.

Submicrometer particulate and particles up to a few micrometers in diameter may be expected to travel considerable distances from the source before being deposited or washed out of the air by natural processes. Particles of one or two micrometers in diameter will behave almost as gas molecules in their mixing and traveling. Thus, one would expect to find molybdenum widespread as a background constituent of air.

The air in three cities has been tested for molybdenum content.[19] The average concentration was 0.013 micrograms/m^3. The particulate containing the molybdenum had an average diameter of 1.16 micrometers,

and the distribution of sizes followed a normal aerosol distribution. About 70 percent of the particulate was contained in particles less than 2 micrometers.

Molybdenum may be a moderately toxic material, although, at present, the evidence is not well developed. It is reported that cattle in the vicinity of a western molybdenum plant were recently found to be suffering from an unusual ailment, and a cause-and-effect relationship was implied.[5] Flyash which explicitly contained molybdenum was found to be a useful soil additive in growing alafalfa, although the benefit was more likely the change of pH in the soil than due to the molybdenum.[8]

VI. UPDATING OF EMISSIONS ESTIMATES

The following recommendations are made for periodically updating the estimates made in this study:

A. VERIFICATION OF CURRENT ESTIMATES

1. Verify that the principal molybdenum processes, the roasting of concentrate and ferromolybdenum production, are adequately represented by these estimates. If possible, emissions data should be obtained from the molybdenum industry rather than by extrapolation from other processes believed to be similar because of the individual nature of molybdenum and its compounds.

2. The production of steel alloys containing molybdenum as an alloying ingredient should be investigated to ascertain that the emissions of molybdenum are in fact proportional to the feed of molybdenum. Steel production is a potentially large source of molybdenum emission, if the emission factor should in fact be larger than assumed.

3. Crushed rock, lime, clay, fertilizer, and cement dusts are of sufficient quantity that even slight molybdenum content could be significant. Typical analyses of these dusts should be made for molybdenum content to verify that the content is in fact as low as assumed.

B. PERIODIC REVIEW OF ESTIMATES

1. The Bureau of Mines estimates for material flow, industry practices, and trends provide the best estimates of the size of the industry.

2. EPA activities are currently generating the best emissions data and should be reviewed using:

   a. Overall industry studies, e.g. Reference (4).

   b. The Source Test Program, in which specific individual plant emissions are measured. This information provides

emission factors for specific examples of typical, industrial operations and also provides some analyses of the particulate, usually including trace metal content and particle size.

c. NEDS (National Emissions Data System) is steadily being enlarged and improved. This system can provide emission factors for specific plants and plant operations, the type of particulate control equipment in use, and the actual, or estimated, control efficiency. The system may eventually be expanded to include description of the emissions.

3. The molybdenum industry should be consulted for its opinion and suggestions on the most recently published estimates. This may be best accomplished by interviewing the Molybdenum Commodity Specialist, Division of Non-ferrous Metals, Bureau of Mines in Washington; or by interviewing one or more of the principal companies in the industry.

4. The literature should be reviewed, using (a) industrial views as published from time to time in Chemical Engineering, for example, and (b) evironmental views as summarized in Pollution Abstracts, for example.

5. Individual companies or plants may be approached for opinions, data, or cooperative tests of their own operations. This is a difficult approach to the problem of obtaining fresh information due to the natural reluctance of the plants to discuss environmental problems. However, data thus obtained have a relatively high degree of reliability.

6. State agencies in which specific plants are located may be able to provide useful information, and should be contacted.

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